PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-183605
(43)Date of publication of application : 15.07.1997

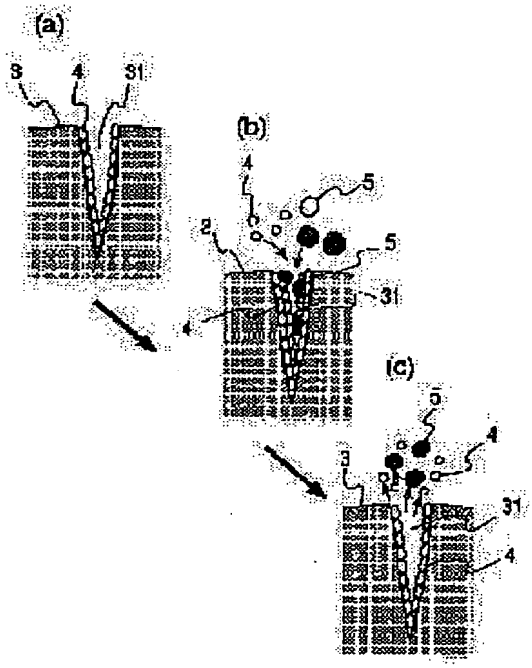
(51)Int.Cl. C01B 31/08
B01J 20/20
F02M 25/08

(21)Application number : 07-353980
(22)Date of filing : 28.12.1995

(71)Applicant : NIPPON SOKEN INC
(72)Inventor : ITAKURA HIDEAKI
KATO NAOYA
YOSHINAGA TORU
KOHAMA TOKIO
AZEGAMI KATSUO

(54) DEGRADATION RESISTING ACTIVATED CARBON AND ITS PRODUCTION AND CANISTER USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To retard the progress of the degradation of an activated carbon by preventing the adsorption of a high b.p. component to a 1st layer of fine pore in the activated carbon.
SOLUTION: A layer of a low b.p. hydrocarbon 4 covering the inside surface of fine pores 31 is provided by adsorbing the low b.p. hydrocarbon 4 at least on the inside surface of the fine pores 31 of the activated carbon 3 having many fine pores 31 on the surface. When the activated carbon 3 is used as an adsorbing material for a canister, a hardly releasable high b.p. component is prevented from being adsorbed to the 1st layer to suppress the decrease of the volume of the fine pores due to the deposition of the high b.p. component, thus to sustain the adsorption capacity.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Degradation-proof nature activated carbon characterized by the thing of the activated carbon which has much pores on a front face for which make a low-boiling point hydrocarbon stick to a pore internal surface at least, and it comes to form a pore internal surface the layer of a wrap low-boiling point hydrocarbon.
[Claim 2] The manufacture approach of the degradation-proof nature activated carbon characterized by consisting of a process to which contact activated carbon in the gas of a low-boiling point hydrocarbon, and a low-boiling point hydrocarbon is made to stick all over the front face of activated carbon, and a process which the obtained activated carbon is contacted to air and removes the low-boiling point hydrocarbon of the front face except the pore internal surface of activated carbon.
[Claim 3] The canister which it is filled up with degradation-proof nature activated carbon according to claim 1 in a tubed bottle object, and it is open for free passage of the end of a fuel adsorption layer, nothing, and the above-mentioned bottle object into a fuel tank, and makes atmospheric air come to be open for free passage of the other end.
[Claim 4] Claim 1 whose above-mentioned low-boiling point hydrocarbon is a with a carbon number of four or less hydrocarbon thru/or degradation-proof nature activated carbon and the manufacture approach given in three, the canister using it.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to activated carbon excellent in the degradation-proof nature used as adsorption material, its manufacture approach, and the canister using it.
[0002]
[Description of the Prior Art] At the time of a car halt, adsorption maintenance of the fuel which evaporates according to the temperature up of a fuel tank is carried out with the canister filled up with activated carbon, and preventing emission out of a vehicle is performed. At the time of engine performance, it ****s by the atmospheric air introduced in a canister (purge), and the fuel vapor (henceforth vapor) which stuck to activated carbon is sent to an inhalation-of-air system, when an inhalation-of-air system serves as negative pressure.
[0003] By the way, the adsorption capacity force of the activated carbon which is fuel adsorption material declines gradually by the repeat of the adsorption and desorption of vapor. When the amount of the vapor generated in a fuel tank exceeds the adsorption capacity force of the activated carbon in the canister at the time, vapor is emitted outside a vehicle and becomes causes, such as a nasty smell.
[0004] Giving a polarity etc. is performed, in order not to perform processing of what to the activated carbon in a canister, either or to mention the adsorption capacity force to it conventionally. If vapor invades in the pore of activated carbon in the condition, vapor sticks to a pore internal surface first, forms the 1st layer, and carries out sequential adsorption further at the upper layer. In the case of an engine purge, it is desorbed from the component which is sticking to the upper layer.
[0005]
[Problem(s) to be Solved by the Invention] However, in the case of this engine purge, by the 1st layer with comparatively strong association with activated carbon, the adsorbate cannot **** easily, and since desorption is more difficult than a low-boiling point component, especially a high-boiling point component tends to remain in pore. That is, when desorption happens by the 1st layer, it is desorbed from a low-boiling point component, and a high-boiling point component sticks to the hole from which this low-boiling point component escaped and the rate of a high-boiling point component increases to it gradually, degradation of activated carbon advances. And since a high-boiling point component has large molecular weight and its volume occupied in pore is large, it reduces pore volume and makes the adsorption capacity force decline further.
[0006] Thus, when a high-boiling point component remains in the 1st layer, it has become clear that degradation of activated carbon is promoted and the cure which prevents adsorption of the high-boiling point component to the 1st layer is needed. A deer is carried out, and this invention prevents adsorption of a layer [of the pore of activated carbon / 1st] high-boiling point component, and aims at delaying advance of degradation of activated carbon.
[0007]
[Means for Solving the Problem] As this invention person etc. inquired wholeheartedly in order to solve the above-mentioned trouble, and shown in drawing 1 (a), it is the thing of the activated carbon 3 which has much pores 31 on a front face which the low-boiling point hydrocarbon 4 is made to stick to pore 31 internal surface at least, and is established [pore 31 internal surface] for the layer of the wrap low-boiling point hydrocarbon 4, and found out that the activated carbon 3 which has high

resistance to degradation was obtained (claim 1).
[0008] Thus, the high-boiling point component 5, i.e., a high-boiling point hydrocarbon, will stick more than to the 2nd layer by forming the layer of a low-boiling point component in the internal surface of pore 31 beforehand (drawing 1 (b)). It is easily desorbed from the high-boiling point hydrocarbon 5 which is sticking to association between hydrocarbons more than at the 2nd layer since it is weak compared with association with activated carbon 3 (drawing 1 (c)). On the other hand, since the low-boiling point hydrocarbon 4 of the 1st layer is association with activated carbon 3, it will be hard to **** and the high-boiling point hydrocarbon 5 will repeat adsorption and desorption more than by the 2nd layer. Therefore, adsorption of the high-boiling point hydrocarbon 5 to the 1st layer leading to degradation of activated carbon 3 can be prevented, and the speed of reduction of the pore volume by deposition of the high-boiling point hydrocarbon 5 becomes slow. The adsorption capacity force can compare with the former in this way, it can continue for a long time, and degradation can be delayed.
[0009] Thus, after contacting activated carbon in the gas of a low-boiling point hydrocarbon and, making a low-boiling point hydrocarbon adsorb all over the front face of activated carbon as an approach of obtaining the activated carbon by which degradation delay was carried out for example, the obtained activated carbon is contacted to air, there is a method of removing the low-boiling point hydrocarbon of the front face except the pore internal surface of activated carbon, and the layer of a low-boiling point hydrocarbon can be easily formed only in a pore internal surface (claim 2).
[0010] Moreover, the canister excellent in endurance is realizable by applying the degradation-proof nature activated carbon obtained as mentioned above to a canister. In this case, what is necessary is to be filled up with degradation-proof nature activated carbon 3 in the tubed bottle object 1, to open the end of the fuel adsorption layer 2, nothing, and the above-mentioned bottle object 1 for free passage into a fuel tank, to make atmospheric air open the other end for free passage, and just to constitute a canister, as shown in drawing 3 (claim 3). In addition, it is desirable for the low-boiling point hydrocarbon made to stick to activated carbon to be specifically a with a carbon number of four or less hydrocarbon (claim 4).
[0011]
[Embodiment of the Invention] Hereafter, this invention is explained based on a drawing. An example of the canister structure which makes adsorption material the degradation-proof nature activated carbon of this invention is shown in drawing 3 , and the atmospheric-air port 12 which the tank port 11 which is open for free passage to one end face (left end side of drawing) in the fuel tank of figure abbreviation opens for free passage to atmospheric air at other end faces (right end side of drawing) is established in the cylindrical cup object 1 of both-ends closing. In the above-mentioned bottle object 1, a right-and-left both-ends side is approached, the bridgewalls 13 and 14 which have many through-holes are formed, respectively, among these bridgewalls 13 and 14, it fills up with the degradation-proof nature activated carbon 3 of this invention, and the fuel adsorption layer 2 is formed.
[0012] In this invention, as the above-mentioned activated carbon 3, as shown in drawing 1 (a), the activated carbon which formed the layer of the low-boiling point hydrocarbon 4 in the internal surface of pore 31 at least is used. a with a carbon number of four or less which is a gas in ordinary temperature (20 degrees C) as a low-boiling point hydrocarbon 4 here low-boiling point hydrocarbon -- butane etc. can specifically use it suitably. The high-boiling point hydrocarbon from which it is hard to be desorbed prevents sticking to the 1st layer of pore 31 internal surface, and degrading activated carbon that the layer of this low-boiling point hydrocarbon 4 should just be formed in extent which the internal surface of pore 31 does not expose very thinly. If the layer of the low-boiling point hydrocarbon 4 becomes thick, since effective pore volume will decrease, the thinner possible one of the layer of the low-boiling point hydrocarbon 4 is desirable.
[0013] In order to obtain the degradation-proof nature activated carbon of this invention, commercial activated carbon is enough contacted in the gas of a low-boiling point hydrocarbon, and a low-boiling point hydrocarbon is made to adsorb all over the front face of activated carbon as the 1st process first. What is necessary is to enclose activated carbon in the canister container 1 of drawing 3 , and just to specifically introduce the gas of the low-boiling point hydrocarbon 4 in a container 1 from a tank port 11. The amount of installation of the gas of the low-boiling point hydrocarbon 4 can

be made into extent in which the low-boiling point hydrocarbon 4 carries out a breakthrough from the atmospheric-air port 12 of a container 1, and, thereby, can make a low-boiling point hydrocarbon adsorb uniformly all over the front face of activated carbon here.

[0014] Next, the obtained activated carbon is contacted to air at the 2nd process, and the low-boiling point hydrocarbon of the front face except the pore internal surface of activated carbon is removed. Specifically, thereby, the low-boiling point hydrocarbon of an activated carbon outside surface is desorbed from the atmospheric-air port 12 that what is necessary is just to introduce the atmospheric air of amount sufficient in a container 1. Moreover, the low-boiling point hydrocarbon of the 2nd more than layer except the 1st layer from which bonding strength on the front face of activated carbon cannot be strongly desorbed easily among the low-boiling point hydrocarbons in pore ****s, and it is discharged from a tank port 11.

[0015] Here, the atmospheric amount of installation (l) is usually made more than activated carbon (capacity l) x300. In this case, what is necessary is to pass atmospheric air (2l., then 2x300=600l.), and just to continue activated carbon capacity temporarily, for 24 minutes, if an atmospheric-air flow rate is 25 l/min. It may be about activated carbon (capacity l) x600 preferably. The activated carbon 3 of drawing 1 which has the layer of the low-boiling point hydrocarbon 4 only in the 1st layer of a pore internal surface in this way is obtained.

[0016] In addition, the manufacture approach of the degradation-proof nature activated carbon of this invention puts commercial activated carbon not only into the above-mentioned approach but into a stirrer, and after putting to a low-boiling point hydrocarbon enough, introducing and stirring a low-boiling point hydrocarbon, the approach of introducing atmospheric air and removing an excessive low-boiling point hydrocarbon can also be used for it. Moreover, although the effectiveness of this invention will be acquired if the layer of the low-boiling point hydrocarbon 4 is formed in activated carbon pore 31 internal surface at least, the low-boiling point hydrocarbon 4 may be sticking to the outside surface of activated carbon.

[0017] drawing 2 -- surface preparation -- carrying out -- **** -- the former -- activated carbon -- three -- ' -- vapor -- adsorbing -- deteriorating -- a situation -- typical -- having been shown -- a thing -- it is -- drawing 2 -- (-- a --) -- an initial state -- activated carbon -- three -- ' -- pore -- 31 -- ' -- inside -- the high-boiling point hydrocarbon 5 with large molecular weight, and the low-boiling point hydrocarbon 4 with small molecular weight -- invading -- the 1st layer of the internal surface -- random -- adsorbing (drawing 2 (b)) .

[0018] Although easily desorbed from (drawing 2 (c)) and the adsorbate of the 2nd more than layer in the case of an engine purge, it is hard to **** and the adsorbate of the 1st layer, especially the high-boiling point hydrocarbon 5 tend to remain. For this reason, when desorption happens by the 1st layer, the rate of the high-boiling point hydrocarbon 5 of the 1st layer increases gradually by being previously desorbed from the low-boiling point hydrocarbon 4, and the high-boiling point hydrocarbon's 5 sticking to that hole from which it escaped, and repeating this. moreover, the high-boiling point hydrocarbon 5 with the large molecule itself -- pore 31' -- since the volume occupied inside is large -- pore 31' of other components -- invasion inside is barred and space (dead space) 311' which cannot demonstrate the adsorption capacity force is built. Thus, by the high-boiling point hydrocarbon 5 which sticks to the 1st layer directly, and dead space 311', degradation will advance quickly.

[0019] On the other hand, since the layer of the low-boiling point hydrocarbon 4 is beforehand formed in the 1st layer when vapor sticks to the activated carbon of this invention shown in drawing 1 (drawing 1 (a)), if adsorption is started from this condition, the high-boiling point hydrocarbon 5 will carry out laminating adsorption one by one more than at the 2nd layer (drawing 1 (b)). In the case of an engine purge, it ****s sequentially from (drawing 1 (c)) and the upper layer, and is easily desorbed from the high-boiling point hydrocarbon 5 which exists more than in the 2nd layer and the 3rd layer. At this time, compared with the adsorbate of the 2nd more than layer, it will be hard to ****, and vapor will stick to the 1st layer combined with activated carbon 3 comparatively strongly again on it. Therefore, the increment in the amount of adsorption of the high-boiling point hydrocarbon 5 of the 1st layer is controlled, and the reduction speed of pore 31 volume becomes slow. In this way, the adsorption capacity force continues for a long period of time, and degradation is delayed.

[0020]
[Example] The trial for checking the effectiveness of this invention using the equipment shown in drawing 4 was performed. Commercial activated carbon was enclosed in the canister bottle object 1, and the tank port 11 was connected to the bomb 6 of the commercial butane which is a low-boiling point hydrocarbon component through the regulator 7 and the positive crankcase ventilation valve 8. On the other hand, the atmospheric-air port 12 was connected to the breakthrough detection concentration meter 9. Here, the magnitude of a bottle object 1 is 80mm in diameter [of 50mm] x die length, and the die length of the fuel adsorption layer 2 set 60mm and activated carbon capacity to 120 cc.
[0021] The commercial butane was introduced by the flow rate 1 - 3 l/min from the tank port 11 in the bottle object 1, and butane was made to stick to an activated carbon front face using the above-mentioned equipment. Installation of a commercial butane was suspended for the commercial butane a sink and after that until the commercial-butane concentration detected in the above-mentioned breakthrough detection densimeter 9 exceeded 2 capacity %. Next, atmospheric air was introduced in the bottle object 1 from the atmospheric-air port 12, activated carbon was contacted to air, and the butane of the front face except a pore internal surface was removed. The atmospheric amount of installation was made into activated carbon capacity 0.12(l) x600=72(l).
[0022] Thus, the adsorption performance evaluation of the canister which makes adsorption material the activated carbon which made butane stick to a pore internal surface was performed. After introducing the gasoline steam and carrying out breakthrough adsorption from the tank port 11 of the above-mentioned bottle object 1, the evaluation trial introduced the atmospheric air of activated carbon (capacity l) x600 from the atmospheric-air port 12, performed air purging, and was performed [make / into 1 cycle / this] by repeating the same trial up to 150 cycle. It is shown in drawing 5 by making relation of the number of cycles, the amount of HC survival in a canister, and the rate of degradation into an example. Moreover, commercial activated carbon was enclosed with the canister as it was for the comparison, the same trial was performed, and it wrote together to drawing 5 by making a result into the conventional example.
[0023] In the conventional example, the amount of HC survival increases quickly, and advance of degradation is quick so that clearly [drawing 5]. On the other hand, when the degradation-proof nature activated carbon of this invention is used, the method of survival of HC is loose and, moreover, there are few the amounts far compared with the former. Therefore, advance of degradation of activated carbon is controlled by this invention, and it turns out that the endurance of a canister can be improved greatly.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 (a) - (c) is a mimetic diagram for explaining the adsorbed state of the vapor to the degradation-proof nature activated carbon of this invention.
[Drawing 2] Drawing 2 (a) - (c) is a mimetic diagram for explaining the adsorbed state of the vapor to conventional activated carbon.
[Drawing 3] Drawing 3 is the whole canister outline sectional view which used the degradation-proof nature activated carbon of this invention as adsorption material.
[Drawing 4] Drawing 4 is drawing showing the adsorption performance-evaluation test method of the canister in an example.
[Drawing 5] Drawing 5 is drawing showing the adsorption performance-evaluation test result of the canister in an example.
[Description of Notations]
1 Bottle Object
11 Tank Port
12 Atmospheric-Air Port
2 Fuel Adsorption Layer
3 Activated Carbon
31 Pore
4 Low-boiling Point Hydrocarbon
5 High-boiling Point Hydrocarbon

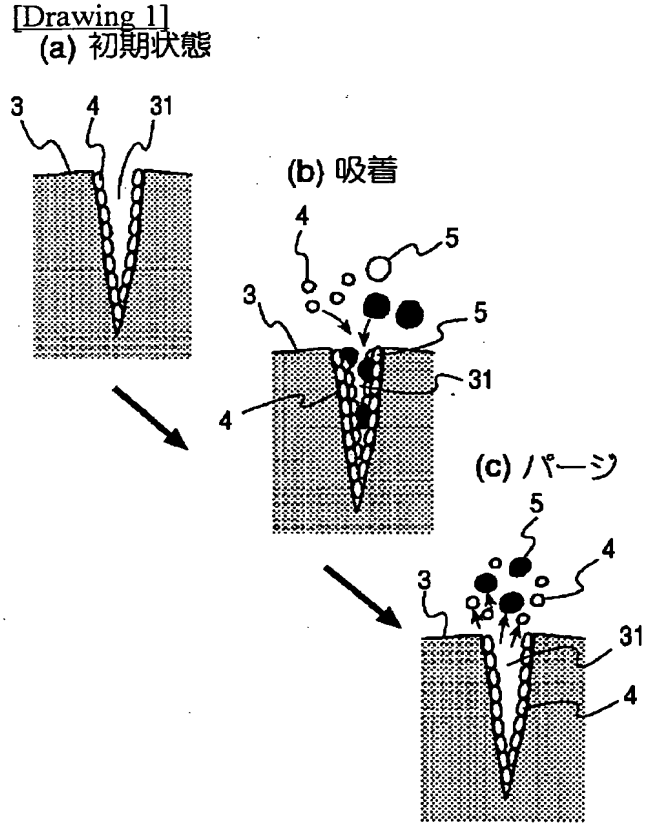
[Translation done.]

* NOTICES *

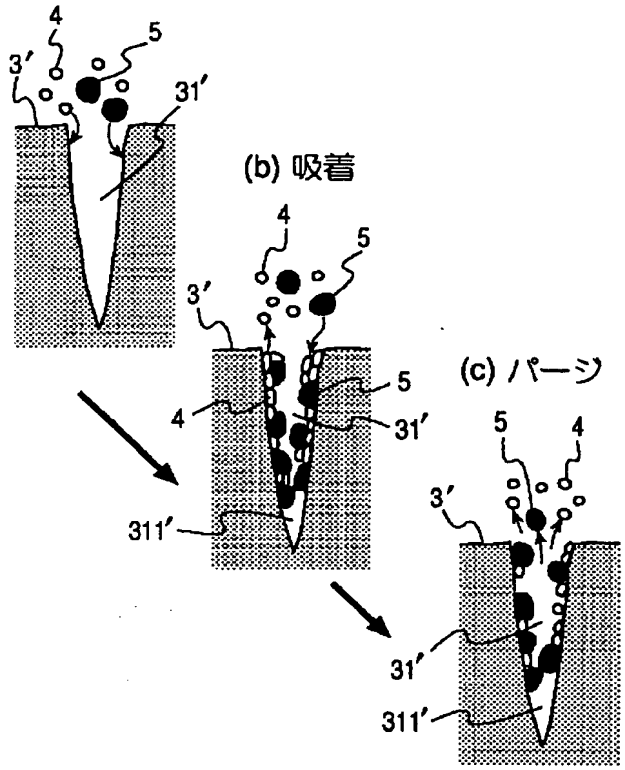
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

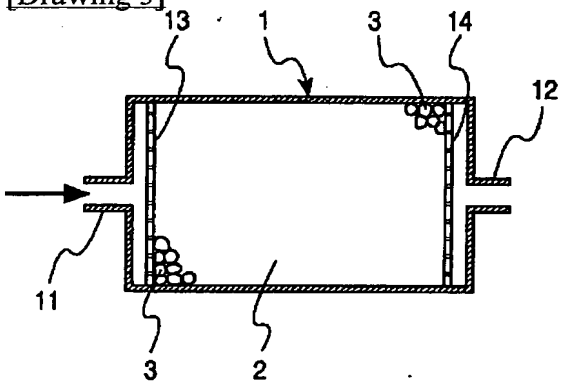
[Drawing 1]



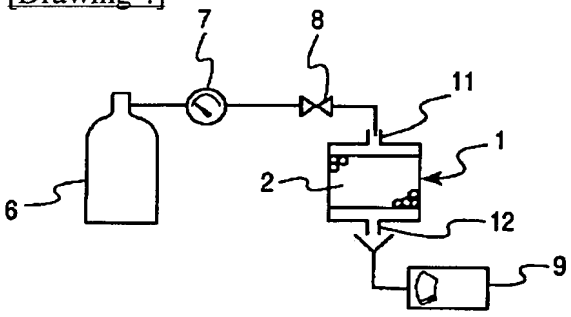
[Drawing 2]



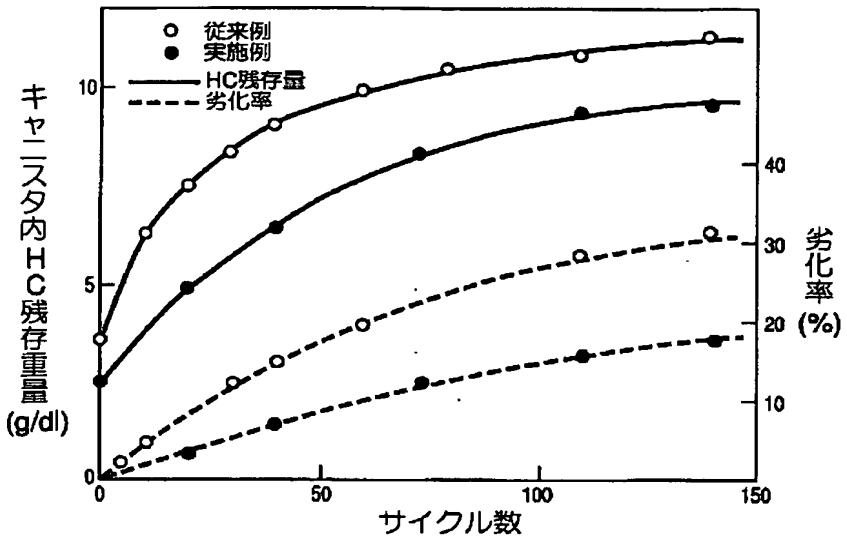
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号

特開平9－183605

(43)公開日　平成９年(1997)７月15日

(51)Int.Cl.[6]	識別記号	庁内整理番号	ＦＩ		技術表示箇所
Ｃ０１Ｂ　31/08			Ｃ０１Ｂ　31/08	Ｚ	
Ｂ０１Ｊ　20/20			Ｂ０１Ｊ　20/20	Ｅ	
Ｆ０２Ｍ　25/08	３１１		Ｆ０２Ｍ　25/08	３１１Ｄ	

審査請求　未請求　請求項の数４　ＦＤ　（全５頁）

(21)出願番号　特願平7－353980

(22)出願日　平成７年(1995)12月28日

(71)出願人　000004695
株式会社日本自動車部品総合研究所
愛知県西尾市下羽角町岩谷14番地

(72)発明者　板倉　秀明
愛知県西尾市下羽角町岩谷14番地　株式会社日本自動車部品総合研究所内

(72)発明者　加藤　直也
愛知県西尾市下羽角町岩谷14番地　株式会社日本自動車部品総合研究所内

(72)発明者　吉永　融
愛知県西尾市下羽角町岩谷14番地　株式会社日本自動車部品総合研究所内

(74)代理人　弁理士　伊藤　求馬

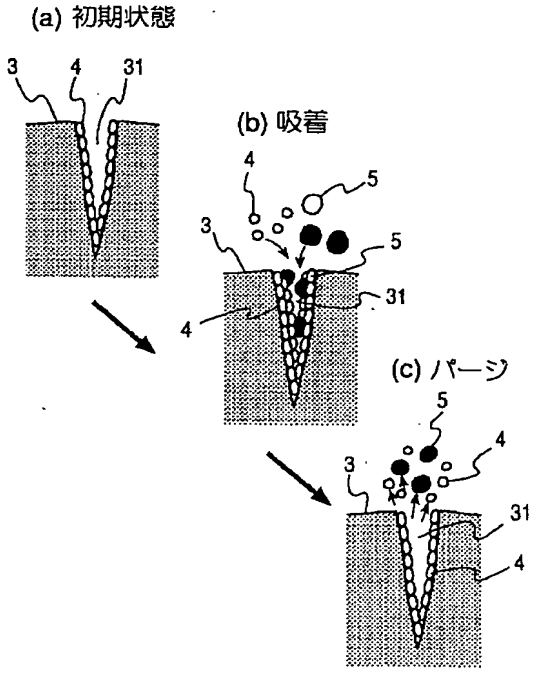
最終頁に続く

(54)【発明の名称】　耐劣化性活性炭とその製造方法およびそれを用いたキャニスタ

(57)【要約】

【課題】　活性炭の細孔第１層への高沸点成分の吸着を防止して、活性炭の劣化の進行を遅らせることを目的とする。

【解決手段】　表面に多数の細孔３１を有する活性炭３の、少なくとも細孔３１内表面に低沸点炭化水素４を吸着せしめて、細孔３１内表面を覆う低沸点炭化水素４の層を設ける。この活性炭３をキャニスタ用の吸着材とすれば、脱離しにくい高沸点成分が第１層に吸着することが防止され、高沸点成分の堆積による細孔容積の減少が抑制されて吸着能力が持続する。



1

【特許請求の範囲】

【請求項１】　表面に多数の細孔を有する活性炭の、少なくとも細孔内表面に低沸点炭化水素を吸着せしめて、細孔内表面を覆う低沸点炭化水素の層を形成してなることを特徴とする耐劣化性活性炭。

【請求項２】　活性炭を低沸点炭化水素のガスと接触させて活性炭の表面全面に低沸点炭化水素を吸着させる工程と、得られた活性炭を空気と接触させて、活性炭の細孔内表面を除く表面の低沸点炭化水素を除去する工程とからなることを特徴とする耐劣化性活性炭の製造方法。

【請求項３】　請求項１記載の耐劣化性活性炭を筒状容器体内に充填して燃料吸着層となし、上記容器体の一端を燃料タンクに、他端を大気に連通せしめてなるキャニスタ。

【請求項４】　上記低沸点炭化水素が炭素数４以下の炭化水素である請求項１ないし３記載の耐劣化性活性炭とその製造方法およびそれを用いたキャニスタ。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、吸着材として使用される耐劣化性に優れた活性炭とその製造方法、およびそれを用いたキャニスタに関する。

【０００２】

【従来の技術】車両停止時、燃料タンクの昇温により蒸発する燃料を、活性炭を充填したキャニスタで吸着保持し、車外への放出を防止することが行われている。活性炭に吸着した燃料蒸気（以下、ベーパという）は、エンジン作動時に、吸気系が負圧となることによりキャニスタ内に導入される大気によって脱離（パージ）し、吸気系に送られる。

【０００３】ところで、燃料吸着材である活性炭の吸着能力は、ベーパの吸脱着の繰り返しにより徐々に低下していく。燃料タンクで発生するベーパの量がその時点におけるキャニスタ内の活性炭の吸着能力を越える場合には、ベーパが車外に放出されて異臭等の原因となる。

【０００４】従来、キャニスタ内の活性炭には、何の処理も行われないか、吸着能力を挙げるために極性を付与する等が行われている。その状態でベーパが活性炭の細孔内に侵入すると、ベーパはまず細孔内表面に吸着して第１層を形成し、さらにその上層に順次吸着していく。エンジンパージの際には、上層に吸着している成分から脱離する。

【０００５】

【発明が解決しようとする課題】しかしながら、このエンジンパージの際、活性炭との結合が比較的強い第１層では吸着物が脱離しにくく、特に、高沸点成分は低沸点成分よりも脱離が困難であるため、細孔内に残存しやすい。つまり、第１層で脱離が起こる場合には、低沸点成分から脱離し、この低沸点成分が抜けた穴に、高沸点成分が吸着して、次第に高沸点成分の割合が増加することにより、活性炭の劣化が進行していく。しかも、高沸点成分は分子量が大きく、細孔内に占める体積が大きいため、細孔容積を減らし、吸着能力をさらに低下させることになる。

2

【０００６】このように、第１層に高沸点成分が残存することにより活性炭の劣化が促進されることが判明しており、第１層への高沸点成分の吸着を防止する対策が必要となっている。しかして、本発明は、活性炭の細孔第１層への高沸点成分の吸着を防止して、活性炭の劣化の進行を遅らせることを目的とするものである。

【０００７】

【課題を解決するための手段】本発明者等は上記問題点を解決するために鋭意検討し、図１（ａ）に示すように、表面に多数の細孔３１を有する活性炭３の、少なくとも細孔３１内表面に低沸点炭化水素４を吸着せしめて、細孔３１内表面を覆う低沸点炭化水素４の層を設けることで、劣化に対し高い耐性を有する活性炭３が得られることを見出した（請求項１）。

【０００８】このように、予め細孔３１の内表面に低沸点成分の層を形成しておくことで、高沸点成分、すなわち高沸点炭化水素５は第２層以上にのみ吸着することになる（図１（ｂ））。炭化水素間の結合は、活性炭３との結合に比べて弱いため、第２層以上に吸着している高沸点炭化水素５は容易に脱離する（図１（ｃ））。一方、第１層の低沸点炭化水素４は活性炭３との結合であるため、脱離されにくく、高沸点炭化水素５は第２層以上で吸脱着を繰り返すことになる。従って、活性炭３の劣化の原因となっている第１層への高沸点炭化水素５の吸着を防止でき、高沸点炭化水素５の堆積による細孔容積の減少のスピードが遅くなる。かくして吸着能力が従来に比し長く持続し、劣化を遅延させることができる。

【０００９】このように劣化遅延された活性炭を得る方法としては、例えば、活性炭を低沸点炭化水素のガスと接触させて活性炭の表面全面に低沸点炭化水素を吸着させた後、得られた活性炭を空気と接触させて、活性炭の細孔内表面を除く表面の低沸点炭化水素を除去する方法があり、細孔内表面のみに容易に低沸点炭化水素の層を形成することができる（請求項２）。

【００１０】また、上記のようにして得られた耐劣化性活性炭をキャニスタに適用することで、耐久性に優れたキャニスタを実現することができる。この場合、図３に示すように、筒状容器体１内に耐劣化性活性炭３を充填して燃料吸着層２となし、上記容器体１の一端を燃料タンクに、他端を大気に連通せしめてキャニスタを構成すればよい（請求項３）。なお、活性炭に吸着させる低沸点炭化水素は、具体的には炭素数４以下の炭化水素であることが望ましい（請求項４）。

【００１１】

【発明の実施の形態】以下、本発明を図面に基づいて説明する。図３には本発明の耐劣化性活性炭を吸着材とす

るキャニスタ構造の一例を示し、両端閉鎖の円筒状容器体１には、一方の端面（図の左端面）に図略の燃料タンクに連通するタンクポート１１が、他の端面（図の右端面）に大気に連通する大気ポート１２が設けてある。上記容器体１内には、左右両端面に近接して、多数の通孔を有する仕切り壁１３、１４がそれぞれ設けてあり、これら仕切り壁１３、１４の間に本発明の耐劣化性活性炭３が充填されて燃料吸着層２を形成している。

【００１２】本発明では上記活性炭３として、図１（ａ）に示すように、少なくとも細孔３１の内表面に低沸点炭化水素４の層を形成した活性炭を用いる。ここで、低沸点炭化水素４としては、常温（２０℃）で気体である炭素数４以下の低沸点炭化水素、具体的にはブタン等が好適に使用できる。この低沸点炭化水素４の層は、細孔３１の内表面が露出しない程度に、ごく薄く形成されていればよく、脱離しにくい高沸点炭化水素が、細孔３１内表面の第１層に吸着して活性炭を劣化させるのを防止する。低沸点炭化水素４の層が厚くなると、有効な細孔容積が減少するので、低沸点炭化水素４の層はできるだけ薄い方が好ましい。

【００１３】本発明の耐劣化性活性炭を得るには、まず、第１工程として、市販の活性炭を低沸点炭化水素のガスと十分接触させ、活性炭の表面全面に低沸点炭化水素を吸着させる。具体的には、活性炭を図３のキャニスタ容器１内に封入し、タンクポート１１より容器１内に低沸点炭化水素４のガスを導入すればよい。ここで、低沸点炭化水素４のガスの導入量は、容器１の大気ポート１２から低沸点炭化水素４が破過してくる程度とし、これにより活性炭の表面全面に満遍なく低沸点炭化水素を吸着させることができる。

【００１４】次に、第２工程で、得られた活性炭を空気と接触させて、活性炭の細孔内表面を除く表面の低沸点炭化水素を除去する。具体的には、大気ポート１２から容器１内に十分な量の大気を導入すればよく、活性炭外表面の低沸点炭化水素がこれにより脱離する。また、細孔内の低沸点炭化水素のうち、活性炭表面との結合力が強く脱離しにくい第１層を除く、第２層以上の低沸点炭化水素が脱離してタンクポート１１より排出される。

【００１５】ここで、大気の導入量（ｌ）は、通常、活性炭容量（ｌ）×３００以上とする。この場合、仮に活性炭容量を２１とすれば、２×３００＝６００１の大気を流すことになり、大気流量が２５１／ｍｉｎならば２４分、連続して流せばよい。好ましくは活性炭容量（ｌ）×６００程度とする。かくして細孔内表面第１層のみに低沸点炭化水素４の層を有する図１の活性炭３が得られる。

【００１６】なお、本発明の耐劣化性活性炭の製造方法は、上記方法に限らず、例えば、撹拌器に市販の活性炭を入れて低沸点炭化水素を導入し、撹拌しながら低沸点炭化水素に十分曝した後、大気を導入して余剰の低沸点炭化水素を除去する方法を採用することもできる。また、低沸点炭化水素４の層は、少なくとも活性炭細孔３１内表面に形成されていれば本発明の効果が得られるが、活性炭の外表面に低沸点炭化水素４が吸着していてもかまわない。

【００１７】図２は、表面処理を行っていない従来の活性炭３´にベーパが吸着して劣化していく様子を模式的に示したもので、図２（ａ）の初期状態の活性炭３´の細孔３１´内に、分子量の大きい高沸点炭化水素５と分子量の小さい低沸点炭化水素４が侵入して、その内表面第１層にランダムに吸着する（図２（ｂ））。

【００１８】エンジンパージの際には（図２（ｃ））、第２層以上の吸着物は容易に脱離するが、第１層の吸着物、特に高沸点炭化水素５は脱離しにくく、残存しやすい。このため第１層で脱離が起こる場合には、低沸点炭化水素４から先に脱離し、その抜けた穴に高沸点炭化水素５が吸着して、これを繰り返すことにより、第１層の高沸点炭化水素５の割合が次第に増加する。また、分子自体が大きい高沸点炭化水素５は細孔３１´内に占める体積が大きいため、他の成分の細孔３１´内への侵入を妨げ、吸着能力を発揮できない空間（デッドスペース）３１１´をつくる。このように第１層に直接吸着する高沸点炭化水素５とデッドスペース３１１´により、劣化が急速に進行することになる。

【００１９】これに対し、図１に示す本発明の活性炭にベーパが吸着する場合には、予め第１層に低沸点炭化水素４の層が形成されているため（図１（ａ））、この状態から吸着を開始すると高沸点炭化水素５は第２層以上に順次、積層吸着する（図１（ｂ））。エンジンパージの際には（図１（ｃ））、上層から順に脱離していき、第２層、第３層以上にのみ存在する高沸点炭化水素５は容易に脱離する。この時、活性炭３と比較的強く結合している第１層は、第２層以上の吸着物に比べて脱離しにくく、その上に再度ベーパが吸着していくことになる。よって、第１層の高沸点炭化水素５の吸着量の増加が抑制され、細孔３１容積の減少スピードが遅くなる。かくして、吸着能力が長期間持続し、劣化が遅延される。

【００２０】

【実施例】図４に示す装置を用いて本発明の効果を確認するための試験を行った。市販の活性炭をキャニスタ容器体１内に封入し、タンクポート１１を低沸点炭化水素成分であるブタンガスのボンベ６に、レギュレータ７、流量調整バルブ８を介して接続した。一方、大気ポート１２を破過検出濃度計９に接続した。ここで、容器体１の大きさは、直径５０ｍｍ×長さ８０ｍｍであり、燃料吸着層２の長さは６０ｍｍ、活性炭容量は１２０ｃｃとした。

【００２１】上記装置を用いて、容器体１内にタンクポート１１よりブタンガスを流量１～３１／ｍｉｎで導入し、活性炭表面にブタンを吸着させた。上記破過検出濃

5　　6

度計９において検出されるブタンガス濃度が２容量%を越えるまでブタンガスを流し、その後、ブタンガスの導入を停止した。次に、大気ポート１２から容器体１内に大気を導入して活性炭を空気と接触させ、細孔内表面を除く表面のブタンを除去した。大気の導入量は、活性炭容量０．１２（１）×６００＝７２（１）とした。

【００２２】このようにして細孔内表面にブタンを吸着させた活性炭を吸着材とするキャニスタの吸着性能評価を行った。評価試験は、上記容器体１のタンクポート１１よりガソリン蒸気を導入して破過吸着させた後、大気ポート１２から活性炭容量（１）×６００の大気を導入してエアパージを行い、これを１サイクルとして、１５０サイクルまで同様の試験を繰り返し行った。サイクル数とキャニスタ内のＨＣ残存量、劣化率の関係を実施例として図５に示す。また、比較のため市販の活性炭をそのままキャニスタに封入して同様の試験を行い、結果を従来例として図５に併記した。

【００２３】図５に明らかなように、従来例ではＨＣ残存量が急速に増加し、劣化の進行が速い。これに対し、本発明の耐劣化性活性炭を用いた場合には、ＨＣの残存のしかたが緩やかでしかもその量は従来に比べてはるかに少ない。よって、本発明により活性炭の劣化の進行を＊抑制して、キャニスタの耐久性を大きく向上できることがわかる。

【図面の簡単な説明】

【図１】図１（ａ）～（ｃ）は本発明の耐劣化性活性炭へのベーパの吸着状態を説明するための模式図である。

【図２】図２（ａ）～（ｃ）は従来の活性炭へのベーパの吸着状態を説明するための模式図である。

【図３】図３は本発明の耐劣化性活性炭を吸着材として用いたキャニスタの全体概略断面図である。

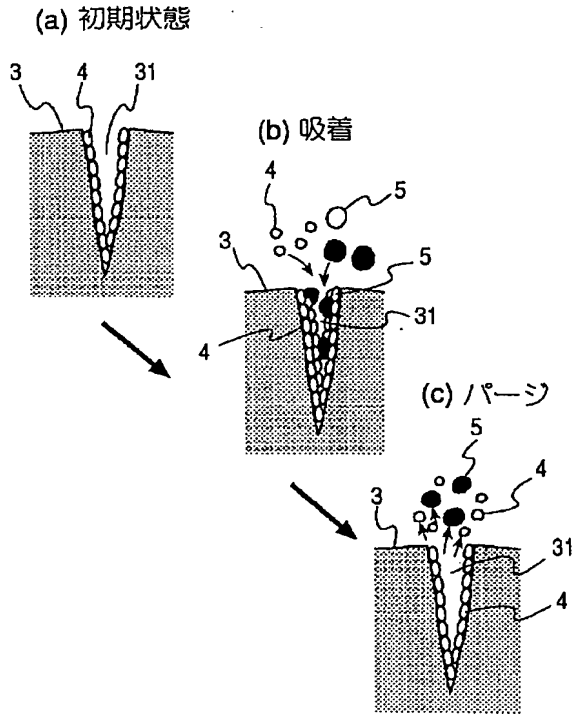
【図４】図４は実施例におけるキャニスタの吸着性能評価試験方法を示す図である。

【図５】図５は実施例におけるキャニスタの吸着性能評価試験結果を示す図である。

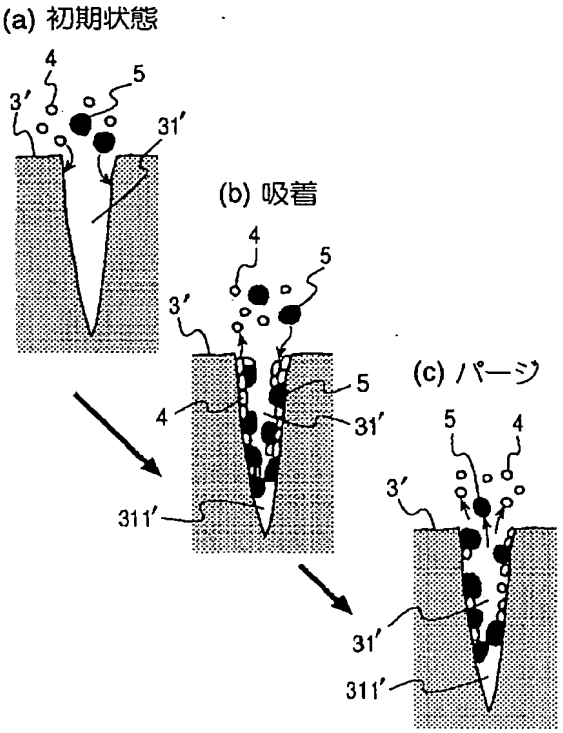
【符号の説明】

１　容器体
１１　タンクポート
１２　大気ポート
２　燃料吸着層
３　活性炭
３１　細孔
４　低沸点炭化水素
５　高沸点炭化水素

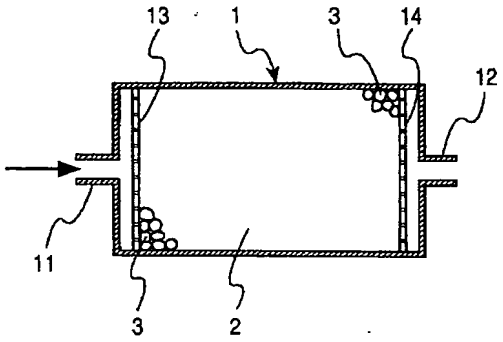
【図１】



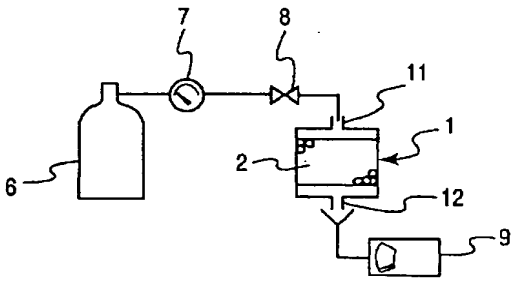
【図２】



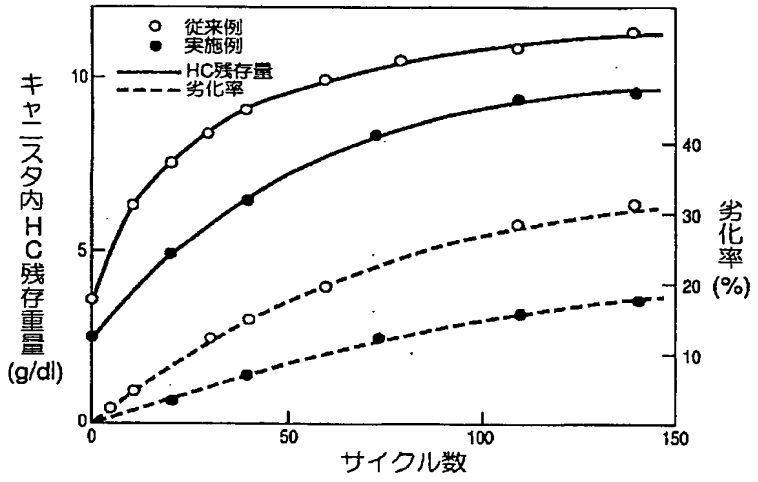
【図３】



【図４】



【図５】



フロントページの続き

(72)発明者　小浜　時男
愛知県西尾市下羽角町岩谷14番地　株式会社日本自動車部品総合研究所内

(72)発明者　畔上　勝男
愛知県西尾市下羽角町岩谷14番地　株式会社日本自動車部品総合研究所内